

PATENT SPECIFICATION

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378,372

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Complete Accepted: July 29, 1932.

COMPLETE SPECIFICATION.



Improvements in or relating to the Production of Margarine and like Edible Fat Emulsions.

We, THE EMULSOL CORPORATION, a corporation organised under the laws of the State of Illinois, United States of America, of 59, East Madison Street, Chicago, State of Illinois, United States of America, Assignees of ALBERT KUBA EPSTEIN and BENJAMIN RACZKOWSKI HARRIS, both citizens of the United States of America, of 5, South Wabash Avenue, Chicago, Illinois, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method of producing improved margarine and the like edible fat emulsions, and to the improved margarine or the like edible fat emulsion resulting therefrom.

The principal object of this invention is the production of an improved margarine.

Other objects and features of the invention will be apparent from a consideration of the following detailed description.

The method according to the invention of producing an improved margarine or the like edible fat emulsion comprises including in the emulsion a relatively small quantity of a compound having the capacity of preventing the spattering of margarine during frying, that is, a compound having hydrophile groups and lipophile groups in substantially balanced relationship, and a relatively small quantity of a compound of the kind defined in our Specification No. 378,373 (co-pending Application No. 2945/31). The compounds of the kind defined in our Specification No. 378,373 (co-pending Application No. 2945/31) produce the effect that the cultured milk or other aqueous medium used in the preparation of the emulsion is more stably bound and will not separate by "leaking" or "weeping" under conditions incident to, and during, the manufacture, storage and use of the margarine or the like edible emulsion. For the sake of brevity, the compounds of the kind defined in our said specification will be referred to hereinafter as "anti-weeping" compounds without any intention, however, of inti-

imating that the effect of such compounds is limited to preventing "leakage" or "weeping" of margarine or the like edible emulsions.

These two substances intimately mixed with each other are prepared preferably in a paste form for easy incorporation into the margarine, but the paste may be prepared in various ways, with different consistencies, and with different types of liquids, and the two substances may be brought together in various manners. We have found that we obtain very much better results when these two types of substances are used together in margarine than if they are used separately. Not only is this true, but also, if they are introduced into the margarine after having been intimately admixed beforehand, their joint effect produces a better margarine than if they are used together in the margarine but introduced separately. We are not prepared to explain the reason for this condition, but we shall discuss the same more fully hereinafter.

We have referred to the types of materials used in the preparation, making reference only to two characteristics which they impart in their individual capacities to the margarine. These substances have other marked effects upon the margarine, however, which produce margarine superior in other respects. In the following portions of the specification where these substances are treated separately, some of these features will be made clearer. Other effects of these two types of compounds are described in our Specification No. 378,373 (co-pending Application No. 2945/31) and Specification No. 366,909.

The anti-spattering compounds of the type which we prefer to use are described fully in our prior Specification No. 366,909.

In our prior Specification No. 366,909 we have described a very large number of chemical substances which when suitably introduced into margarine have the capacity when used even in very minute proportions, of markedly reducing or entirely eliminating the spattering which occurs when ordinary types of margarine

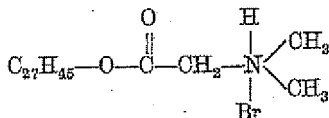
taric, and similar acids, and other groups and molecules with a marked affinity for water.

The compound having the lipophyllic and hydrophyllic groups must possess these groups in such a state of balance as to have an effect in reducing the spattering behavior of margarine, and we have developed a simple test for determining the state of balance between these groups in the molecule. In carrying out the test we place a weighed amount of the margarine containing a definite proportion of the substance the balance in the molecule of which is to be determined, in a small open pan, (an ordinary tablespoon is available for the purpose), and place the same over a Bunsen burner with a properly adjusted flame and with the pan placed at a definite predetermined distance above the burner. Around the Bunsen burner and below the pan is placed a clean blank sheet of paper in such a position that all of the margarine particles which spurt or spatter from the pan during the heating period will be caught by the paper. Using an untreated margarine as a control, the degree of balance in the sample is readily determined by weighing the paper before and after the test or roughly from the size and number of spots found on the paper.

Among compounds which we have used with very good results as anti-spatterers are the following:

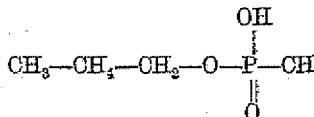
$$\text{C}_{27}\text{H}_{45}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{N}(\text{Br})-\text{Naphthyl}-\text{CH}_3$$

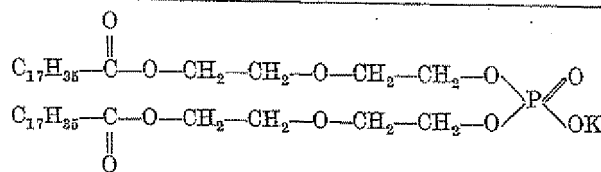
(Carbocholesteroxy methyl quinaldylum
bromide)



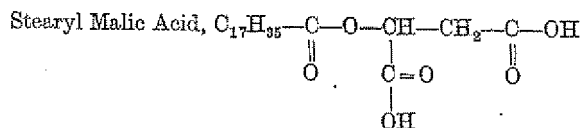
(Cholesteryl dimethylaminoacetate hydrobromide)

75 " Sulphonated " beef tallow
Stearyl diethyleneglycol sulphoacetate, sodium salt
" Stearic Acid Ester of Sucros "



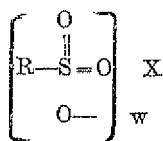


Mannitol Monopalmitate



and many other compounds all having lipophile and hydrophile groups in substantially balanced relationship.

Among the preferred compounds of the invention for use as anti-spattering substances in combination with "anti-weeping" substances are the sulphonic acid derivatives of substances possessing lipophile groups. These substances may be represented by the general formula:



in which "R" is a lipophile radical, "S" represents sulphur linked to a carbon in the radical "R", "O" is oxygen, "X" stands for an innocuous cation, and "w" is a small whole number. Of this class the most valuable compounds for our purpose are the carboxylic esters of sulpho acetic acid, such as the salt of monostearine sulphoacetate. We have found that the most suitable for our purpose is the sodium salt of monostearine sulphoacetate.

As our prior Specification No. 366,909 discloses, lecithin and nitrogenous lecithin-like extracts have been suggested in the past for use with margarine to prevent the spattering thereof. These compounds have not been commercially satisfactory for several reasons. One of the most objectionable characteristics of these compounds in the past was the fact that they liberated from themselves choline and other objectionable amines which had a tendency to impart a fishy taste to substances in which they were used, these lecithin extracts being of a dark color imparted an undesirable color to margarine. It has also been found that some of the objectionable characteristics of lecithin extracts have been due to the pre-

sence of impurities, and for this reason attempts have been made to produce lecithins in a pure state. It appears that the tendency of lecithin to decompose and not only lose its value as an anti-spattering substance, but developing unpleasant taste and odor, is increased by purification. We have found that we can employ lecithin and nitrogenous lecithin-like compounds with some considerable satisfaction when these compounds are admixed with or combined with the "anti-weeping" compounds according to our Specification No. 378,373, 2945 of 1931. The amount of nitrogenous substances required to be used to effect an improvement in a given quantity of margarine is lessened. This is undoubtedly due to the fact that a more complete dispersion of the anti-spattering substance is obtainable when used with the "anti-weeping" compound than when the anti-spattering substance is used alone. For this reason, although we prefer to avoid the use of these nitrogenous compounds in margarine alone, they may be used in accordance with the present invention with satisfactory results, and the present invention is intended to include such use.

The compounds which we use as "anti-weeping" substances in margarine and similar edible emulsions in combination with anti-spattering compounds are, as defined in our Specification No. 378,373 (co-pending Application No. 2945/31), acyl or alkyl derivatives of polyhydroxy compounds wherein the acyl or alkyl group or groups include at least six carbon atoms and are joined through oxygen to the group derived from the polyhydroxy compound in which there remains one or more free hydroxyl groups except in the case of glycerol derivatives in which case there must remain two free hydroxyl groups, and wherein the hydrophylic character of the group derived from the polyhydroxy compound is insufficient to balance the lipophylic character of the acyl or alkyl

group or groups. "Anti-weeping" compounds in accordance with the above definition may be expressed by the general formula

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$$H_w C_x (OH)_y (OR)_z$$
 in which "H", "C" and "O" represent hydrogen, carbon and oxygen respectively, "R" denotes acyl or alkyl groups
10 "w", "x", "y" and "z" are whole numbers greater than zero, "y" being always equal to or greater than "z". The acyl and alkyl groups contain at least six carbons. These compounds are described fully in our prior Specification No. 378,373 (application No. 2945 filed January 29, 1932).

Examples of compounds which can be used in accordance with the present invention are mono-stearic acid ester of glycerine (monostearyl glycerol), mono-palmitic acid ester of glycerol, monocetyl ether of glycerol, monomyristyl glycerol, monolauryl glycerol, monomyristyl diethylene glycol, monomelissyl diethylene glycol, monopalmityl glycerol, mono-oleyl diethylene glycol, mono-oleyl diglycerol, mono-oleyl glycerol, diethylene glycol monostearate, and 1, 6-dilauryl diglycerol. We have found that monostearyl glycerol in particular functions with very great satisfaction in connection with anti-splattering compounds in the production of a margarine improving substance in the form of a paste and is very easily and readily introduced into the margarine in the usual manufacturing processes. Also included in this group are alkyl and acyl derivatives of sugars, such as dextrose, sucrose and derivatives of mannitol, sorbitol, poly-glycerols and similar hydroxy compounds which have sufficient of the hydroxy groups esterified or combined with higher molecular weight lipophile groups to make the compound sufficiently oil wetting but insufficiently water wetting to "balance".

These substances will not produce anti-splattering behaviour in margarine when the margarine is subjected to frying. They will, however, prevent weeping of the margarine by holding the moisture more securely than is possible without their use. They also permit better control of the margarine to produce a uniform product having predetermined substantially constant amount of moisture.

A preferred method of employing the "anti-weeping" and anti-splattering substances together involves formation of a paste. In preparing the paste, we take a mixture of approximately two parts of the "anti-weeping" substance to one part of anti-splattering compound, or even proportions of these two substances, depending upon the char-

acteristics and activity thereof in margarine. This mixture is then emulsified with sweet milk or water in proportions of about three parts of the mixture to approximately four and one-half pounds of the liquid. When the mixture is in a solid or stiff plastic condition at room temperature, as is the case with a mixture of monostearyl glycerol and monostearine sodium sulphate for example, we preliminarily melt the mixture and heat the milk or water to approximately the temperature of the melted mixture. The mixture is then introduced into a beater having a wire loop whip and the hot milk or water is then introduced slowly with constant beating, taking five or ten minutes to introduce all of the milk. Beating is then continued while the substances are allowed to cool to a sufficiently low temperature to produce a paste. If care is not taken during the emulsification or if the paste emulsion is cooled too quickly, the product may be sandy. This does not prevent it from being used, but impairs its effectiveness somewhat. This paste, after cooling, has the consistency of thick cream, the aqueous liquid being in the continuous phase. It can be thinned by the further addition of milk or water, but in any case a product having the desired consistency suitable to permit its addition to the margarine is to be employed.

As to the manner of introducing the substance into the margarine, various processes may be used. We have found, however, that the most satisfactory manner of introducing it into the margarine is to knead or blend the same into the margarine, after it has been crystallized, using any of the usual blending or working equipment, such as a "butter worker". However, the substance may be introduced into the margarine while the latter is in the liquid stage, or it can be dispersed in either the aqueous or oleaginous constituents, but in introducing the substance containing an "anti-weeping" compound or compounds into margarine, certain precautions must be observed, for when the "anti-weeping" compounds are used in margarine they may be productive of inferior results or may lead to difficulties in maintaining the proper emulsion unless handled carefully. The margarines described above are habitually prepared with the oleaginous substances in the continuous phase, and the aqueous substances dispersed therein. There seems to be some tendency for the "anti-weeping" substance to modify the phase structure, and so when introducing the same in the liquid stage, it is not advisable to use more than about 1% 130

thereof. However, if it is introduced after the margarine emulsion has been crystallized and rendered plastic, the amount of this substance can be increased with no injurious results. However, it may be added, the amount used should not be great enough, radically to alter the physical appearance, consistency or texture of the margarine.

One satisfactory method of introducing the mixture of "anti-weeping" substance and anti-spatterer into the liquid emulsion after it has been completed but prior to crystallization of the emulsion, is to thin the previously described paste with milk to approximately the consistency of the liquid emulsion and to disperse the paste in the emulsion with the minimum amount of beating or stirring required for a homogeneous distribution of the paste in the emulsion, that is, with the minimum contact of the "anti-weeping" substance with the emulsion prior to crystallization.

Among the advantages in the use of our anti-spattering substances and "anti-weeping" compounds together is that the action of one of these substances appears to aid the action of the other when they are preliminarily intimately brought together, that is, before their introduction into the margarine. Possibly the dispersion of the two is more thorough when they are so introduced. Since both substances are used in relatively small quantities, obtaining a thorough dispersion is very important if satisfactory results are to be obtained and a uniform margarine product produced.

The mixture of "anti-weeping" substances and anti-spattering substances may also be produced by a method which consists in treating an "anti-weeping" substance of the kind specified in our prior Specification No. 378,373 (Application No. 2945/31) to increase the hydrophylic character of the hydrophile group or groups in the molecules to obtain a mixture of substance having substantially balanced hydrophile and lipophile groups, with "anti-weeping" substance.

We may produce an "anti-weeping" substance as a preliminary step in the production of the anti-spattering substance, and the "anti-weeping" substance being subsequently treated, as for example by "sulphonation", to enhance the hydrophylic function in the molecule. The yield from the process will be found to be a mixture of an "anti-weeping" substance and an anti-spatterer, the anti-weeping substances still being present as innocuous impurities. Instead of employing expensive

processes requiring costly equipment for recovering the anti-spatterer in a pure state, we are able to use the crude yield of the process and obtain better results than if the anti-spatterer were first recovered in a pure state. A specific example of a substance obtainable in this way is a mixture of a monostearic acid ester of glycerol and mono-stearyl sodium sulphate. More particularly, the required mixture may be prepared by esterifying stearic acid with glycerol to produce a mono-stearyl-glycerol, and this product may be treated with sulphuric acid for converting a portion thereof to the monostearyl sulphate. The process yields a mixture of monostearic acid ester of glycerol and monostearyl sulphate.

We may, of course, bring the anti-spattering compounds and the "anti-weeping" compounds together after each has been produced in a relatively pure state, or we may use mixtures of more than one anti-spattering compound with one or more of the "anti-weeping" compounds without departing from the spirit and scope of the invention. All that is necessary to obtain an intimate commingling or mixture of the substances used, and this can be brought about by any suitable mixing or homogenizing apparatus known to those skilled in the art.

Although we described the invention as particularly applicable to margarine, our invention can be used with good results with any of the culinary preparations which consist of emulsions of oleaginous and aqueous constituents, such as the product known as "puff paste" in the baking industry. The term "margarine" therefore, as used in the claims is intended to include all these margarine types of emulsions.

We have described substances for use in our invention as produced in a paste form in which water or fresh milk are used. It is obvious that they may be produced in other forms, and other liquids such as cottonseed oil for example, may be used with them.

It is to be understood that only non-toxic substances will be employed.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of producing improved margarine and the like edible fat emulsions, which comprises including in the emulsion, a relatively small quantity of a compound having the capacity of preventing spattering of the margarine during frying, that is a compound having

- hydrophile groups and lipophile groups in substantially balanced relation, and a relatively small quantity of an "anti-weeping" compound of the type defined in Specification No. 378,373 (application No. 2945/31).
2. A method according to claim 1, wherein the anti-spattering compound employed is a compound of the kind defined in our prior Specification No. 366,909.
3. A method according to claim 1 or 2, wherein said "anti-weeping" and anti-spattering substances are mixed together prior to the introduction thereof into the emulsion.
4. A method according to claim 1, 2 or 3, wherein said substances are emulsified directly with the principal oleaginous and aqueous ingredients of the margarine in the liquid stage, or are formed with a liquid substance into a paste which is kneaded into the margarine after the oleaginous and aqueous substances have been formed into an emulsion and the emulsion has been stabilized to form a solid plastic product.
5. A method according to claim 3, wherein the mixture of anti-weeping and anti-spattering substances is produced by treating an anti-weeping substance of the kind specified in our prior Specification No. 378,373 (application No. 2945/31) to increase the hydrophylic character of the hydrophile group or groups in the molecules to obtain a mixture of substances having substantially balanced hydrophile and lipophile groups, with "anti-weeping" substance.
6. A method of producing an improved margarine or the like edible fat emulsion, substantially as described.
7. A margarine or the like edible fat emulsion, when made by the method claimed and described.
- Dated the 29th day of January, 1931.
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17, John Street, New York, U.S.A.,
Reference has been directed in pursuance of section 7, sub-section 4, of the Patents and Designs Acts, 1907 to 1928, to Specification No. 339,558.